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Fe, Mg and Al distribution in the octahedral sheet of montmorillonites. An infrared study in the OH-bending region

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ABSTRACT: Ten montmorillonites of different origins with variable Fe contents were analysed using transmission IR spectroscopy. Special attention was devoted to the OH-bending region to obtain information about the distribution of octahedral cations. For low to medium Fe contents ($\leqslant$0.56 per Si_8 formula unit), a linear relationship between the position of the δ_{AlFeOH} band and Fe content was observed. Such correlation might be explained by changes in the *cis-trans* occupancy of Fe in the octahedral sheet. Deconvolution of the OH-bending domain allows us to discriminate three components (δ_{AlAlOH}, δ_{AlMgOH} and δ_{AlFeOH}) which are correlated with cation abundances derived from chemical analysis. The relative area of each band can then be compared with theoretical areas calculated assuming a fully random distribution of cations in the octahedral sheet. Using such treatment, eight of the 10 montmorillonites studied presented a nearly randomized octahedral distribution. The two samples from Wyoming were clearly different as they exhibited a strong ordering tendency.

KEYWORDS: montmorillonite, smectite, bentonite, IR spectroscopy, OH-bending region, octahedral cations.

Because of their excellent rheological properties and low cost, bentonite-based muds are used widely in oil drilling and civil engineering. In such applications, the experience of both clay producers and end-users reveals that bentonites of different origins display very different rheological behaviours. These changes in macroscopic properties are maintained when one looks at the properties of the montmorillonite fractions extracted from bentonites. Indeed, recent rheological characterizations carried out in our laboratory on 10 different purified Na-montmorillonite samples from various ore bodies revealed differences in viscosity as large as two orders of magnitude (Vantelon *et al.*, 1999). The origin of such variations is still unknown, but is believed to be linked somehow to the intrinsic properties of the clays. For this reason, we decided to study in detail montmorillonites at various organization scales: substitutions in the crystalline network and their distribution, size and shape of elementary sheets, interactions between platelets and resulting structures, macroscopic behaviour (aggregation, rheology). The role of Fe and of its oxidation state on the crystallinity and swelling behaviour of clay minerals has been studied in numerous papers (e.g. Delineau, 1994; Gaite *et al.*, 1997; Gates *et al.*, 1998; Stucki *et al.*, 2000). It thus seemed that the structural status of this element in smectites could help to explain the observed variations in macroscopic properties.

Infrared (IR) spectroscopy is one of the most effective methods for studying short-range ordering

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in the distribution of cations in phyllosilicates (Fripiat, 1960; Farmer & Russell, 1964; Russell & Fraser, 1994). Indeed, OH IR bands are sensitive to both structural and compositional variations especially in the octahedral sheet (Farmer & Russell, 1964; Farmer, 1974; Cariati *et al.*, 1983; Decarreau *et al.*, 1992; Petit *et al.*, 1992; Bishop *et al.*, 1993, 1999; Cuadros & Altaner, 1998). Hydroxyl vibrations can thus be used as probes for testing the amount and distribution of octahedral Fe (Craciun, 1984; Decarreau *et al.*, 1992; Madejová *et al.*, 1994; Petit *et al.*, 1995; Komadel *et al.*, 1999).

A number of domains contain OH vibrational information: the OH-bending region between 1000 and 750 cm^{-1}, the OH-stretching region between 3750 and 3500 cm^{-1} and the region corresponding to combination and overtones at ~4400 and 7100 cm^{-1}. In the stretching region, the IR spectra of smectites exhibit a broad complex band that reflects the diversity of environments of the hydroxyl groups (AlAlOH, AlMgOH, AlFeOH). Information in this domain can be extracted by using decomposition and curve-fitting procedures (Slonimskaya *et al.*, 1986; Madejová *et al.*, 1994; Besson & Drits, 1997a,b; Drits *et al.*, 1997). Using samples of known chemical composition, and assuming integrated optical densities of the bands to be proportional to the concentration of each type of octahedral hydroxyl, each individual absorption band in the stretching domain can be assigned to a certain pair of octahedral cations coordinated to OH groups. However, in the case of smectites, decomposition of the OH-stretching region is complicated by the presence of components due to residual water that cannot be eliminated, even after heating the sample (Madejová *et al.*, 1994; Komadel *et al.*, 1999; Bishop *et al.*, 1999).

In the region of overtones and combination, the problems associated with the presence of water components are greatly reduced and this spectral range then provides useful information about the octahedral composition of clay minerals (Sposito *et al.*, 1983; Bishop *et al.*, 1999).

In the OH-bending region, the bands associated with each hydroxyl group can be discriminated from each other. Decomposition in this range should then be easier and more efficient, as band assignments are much more straightforward. Furthermore, this domain is not affected by the presence of residual water molecules, which eliminates problems associated with water vapour signal subtraction (Russell, 1980). Finally, this region appears to be more sensitive to octahedral chemical composition than the stretching region (Decarreau *et al.*, 1992). However, as the OH-bending bands are located on the low frequency side of bands corresponding to Si–O–Si stretching, a baseline correction is always necessary. The purpose of this paper is to show that decomposition of the OH-bending bands, taking into account baseline correction, can provide a reasonable estimation of various populations of octahedral sites for dioctahedral smectites with various Fe contents.

MATERIAL AND METHODS

A series of 10 homoionic smectites purified from bentonites of different origins was studied. Clays from Wyoming (SWy1 and SWy2), Texas (STx1), Arizona (SAz1) and Washington (SWa1) were obtained from the Source Clays Repository (University of Missouri) of the Clay Minerals Society. The others, from Bavaria (Bav), China (Chi), Milos (Mil) (Greece), Georgia (Geo) and North Africa (NAf), were obtained from Iko Erbslöh (Germany). There are nine pure montmorillonites and one clay with a nontronitic character, from Washington (SWa1), which can be considered as a peculiar montmorillonite with an extreme Fe content (Komadel *et al.*, 1995). The clays were purified by sedimentation by saturation with Na following three exchanges in molar NaCl solutions. The suspensions were washed with ultra-pure water by centrifugation until chloride-free supernatants were obtained. The final solid products were obtained by air drying. The efficiency of the purification procedure was demonstrated by X-ray diffraction (XRD) which revealed the elimination of crystalline kaolinite, quartz and cristobalite. Chemical analyses of the samples were performed at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Vandœvre-lès-Nancy, France by ICP measurements on a Jobin Yvon 70 quantometer to determine the lattice formulae presented in Table 1. Mössbauer experiments were performed to estimate the oxidation state of Fe in the samples (Table 1). For SWa1, in agreement with results by Murad (1987) and Komadel *et al.* (1995), Mössbauer spectroscopy revealed that 2.9% of the total Fe was bound in poorly crystallized goethite.

Infrared spectra were recorded using a Bruker IFS 55 Fourier transform IR spectrometer at a resolution of 4 cm^{-1} in transmission mode. The

TABLE 1. Origin and structural formulae of the studied montmorillonites.

Na-Montmorillonite	Composition per $O_{20}(OH)_4$
Washington (SWa1)	$(Si_{7.31}Al_{0,69})(Al_{0.90}Mg_{0.23}Fe^{III}_{2.88})Na_{0.92}$
Bavaria (Bav)	$(Si_{7.83}Al_{0.17})(Al_{2.78}Mg_{0.66}Fe^{II}_{0.03}Fe^{III}_{0.53})Na_{0.83}$
Milos (Mil)	$(Si_{7.77}Al_{0.23})(Al_{3.02}Mg_{0.53}Fe^{II}_{0.02}Fe^{III}_{0.43})Na_{0.78}$
Wyoming II (SWy2)	$(Si_{7.76}Al_{0.24})(Al_{3.09}Mg_{0.49}Fe^{III}_{0.46})Na_{0.73}$
Wyoming I (SWy1)	$(Si_{7.74}Al_{0.26})(Al_{3.08}Mg_{0.45}Fe^{III}_{0.42})Na_{0.70}$
Georgia (Geo)	$(Si_{7.83}Al_{0.17})(Al_{2.88}Mg_{0.81}Fe^{II}_{0.07}Fe^{III}_{0.29})Na_{1.00}$
North Africa (NAf)	$(Si_{7.59}Al_{0.41})(Al_{3.28}Mg_{0.44}Fe^{II}_{0.02}Fe^{III}_{0.25})Na_{0.87}$
Arizona (SAz1)	$(Si_{7.95}Al_{0.05})(Al_{2.75}Mg_{1.07}Fe^{III}_{0.17})Na_{1.11}$
Texas (STx1)	$(Si_{7.91}Al_{0.09})(Al_{3.12}Mg_{0.75}Fe^{III}_{0.14})Na_{0.84}$
China (Chi)	$(Si_{7.91}Al_{0.09})(Al_{3.11}Mg_{0.80}Fe^{III}_{0.09})Na_{0.89}$

samples were KBr pellets (1 mg clay for 150 mg KBr) and were observed at room temperature after heating at 150°C for 24 h. Using such pretreatment, most water molecules associated with Na cations can be removed without damaging the clay structure (Pelletier, 1999). The OH-bending vibration positions were deduced from the experimental spectra. For the decomposition procedure, a baseline correction was applied to subtract the ν_{SiO} contribution between 1030 and 730 cm^{-1} (Fig. 1). The baseline was the same for all samples. The corrected spectra were fitted, using at least three components, by a combination of symmetrical Gaussian-Lorentzian curves. The fitting technique is based on the Levenberg-Marquardt method, an algorithm of non-linear curve fitting, provided by Bruker in the OPUS software.

RESULTS AND DISCUSSION

OH-stretching region: 3750–3500 cm^{-1}

The IR spectra in the OH-stretching domain between 3800 and 3500 cm^{-1} are plotted in Fig. 2. All spectra exhibit broad features with maxima located at ~3630–3637 cm^{-1} except for the Fe-rich smectite (SWa1), where the maximum is observed at ~3550 cm^{-1}. Such a position can be assigned to

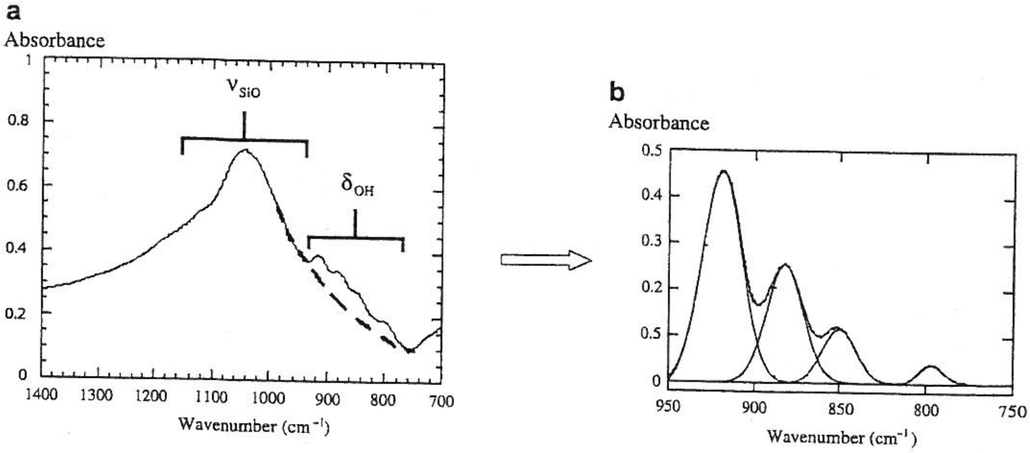

FIG. 1. Treatment procedure of the IR spectra in the OH-bending region. (*a*) Baseline subtraction. (*b*) Deconvolution.

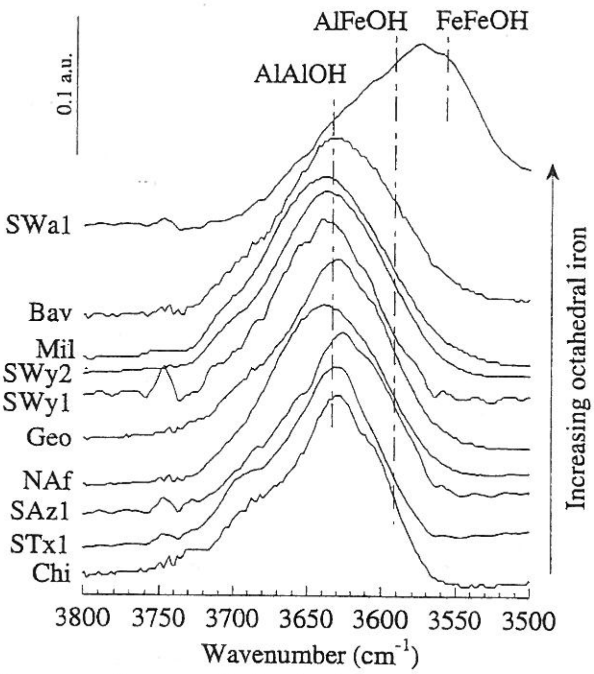

FIG. 2. Transmission IR spectra of montmorillonites in the range of OH-stretching (3800–3500 cm^{-1}) after heating at 150°C.

ν_{FeFeOH} (Madejová *et al.*, 1994; Petit *et al.*, 1995; Komadel *et al.*, 1999; Bishop *et al.*, 1999). A shoulder can be observed on the low frequency side of the OH-stretching band for montmorillonites from China and Texas (Chi and STx1). In general the bands tend to broaden with increasing octahedral Fe^{3+} content, as reported by Farmer (1974) and Craciun (1984). Using synthetic smectites with increasing Fe content, Petit *et al.* (1995) showed a correlation between the amount of Fe in the octahedral sheet and the intensity of the ν_{AlFeOH} (3596 cm^{-1}) and ν_{FeFeOH} (3556 cm^{-1}) bands. The broadening observed in our experimental spectra could then be assigned to the increase of the ν_{AlFeOH} component at 3596–98 cm^{-1} (Petit *et al.*, 1995; Komadel *et al.*, 1999).

OH-bending region: 1000–600 cm^{-1}

In agreement with other results in the literature (Table 2), three major bands, δ_{AlAlOH} at 917–911 cm^{-1}, δ_{AlFeOH} at 878–879 cm^{-1} and δ_{AlMgOH} at 848–838 cm^{-1} were observed for all the spectra (Fig. 3). For the Washington sample, two additional bands were observed at 820 and 786 cm^{-1} (Fig. 3). The band at 820 cm^{-1} can be assigned to δ_{FeFeOH} (Farmer, 1974; Goodman *et al.*, 1976; Petit *et al.*, 1995) and that at 786 cm^{-1} to δ_{FeMgOH} (Goodman *et al.*, 1976; Petit *et al.*, 1995). Finally, all the spectra, except SWa1, exhibit a band at ~795 cm^{-1} which can be assigned to δ_{SiO} in quartz or cristobalite (Craciun, 1984), despite the absence of the significant doublet generally observed for quartz (799 and 779 cm^{-1}). Indeed, regardless of the care taken in the purification procedure, most smectite clays still contain colloidal silica impurities as revealed by detailed TEM experiments (Bérend, 1991). In the same way, Russell & Fraser (1994) assigned a similar band to a platy form of tridymite in a montmorillonite (Wilson *et al.*, 1974).

No MgMg pairs were detected, in agreement with previous studies, the Mg^{2+} content being too low to assume a detectable δ_{MgMgOH} absorption band (Farmer, 1974; Madejová *et al.*, 1994; Cuadros *et al.*, 1999).

When plotted as a function of the content of octahedral ferric Fe, the position of the δ_{AlFeOH} band exhibits a decrease in wavenumber from 886.5 to 874.5 cm^{-1} (Fig. 4) as already observed (Russell &

TABLE 2. Assignments for the OH-bending bands in clay minerals (published in the literature).

Position (cm^{-1})	Assignment	Source	Samples
935	δ_{AlTiOH}	Cuadros & Altaner (1998)	Mixed-layer illite-smectite
915	δ_{AlAlOH}	Farmer (1974)	Dioctahedral species
890	δ_{AlFeOH}	Farmer (1974)	Montmorillonites
850	δ_{FeFeOH}	Stubican & Roy (1961)	Nontronites
	δ_{AlFeOH}	Goodman *et al.* (1976)	Nontronites
	$\nu_{Si\text{-}O}$	Russell *et al.* (1979)	Nontronites
840	δ_{AlMgOH}	Farmer (1974)	Smectites
		Russell & Fraser (1994)	
820	δ_{FeFeOH}	Farmer (1974)	Nontronites
		Goodman *et al.* (1976)	
795	δ_{SiO} quartz	Craciun (1984)	Montmorillonites
	δ_{FeFeOH}	Cuadros *et al.* (1998)	Fe-rich samples
785	δ_{FeMgOH}	Goodman *et al.* (1976)	Nontronites

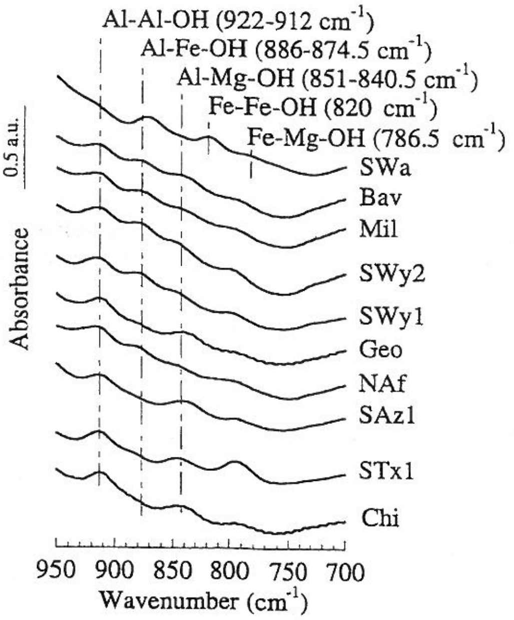

FIG. 3. Transmission IR spectra of montmorillonites in the range of OH-bending (950–700 cm^{-1}).

Fraser, 1994). In the case of nontronites, Goodman *et al.* (1976) showed similar trends. The most complete study dealing with the correlation between Fe content in montmorillonite and δ_{AlFeOH} position was carried out by Craciun (1984). He found a linear relation between these two parameters and suggested that the absorption band at 870 cm^{-1} cannot be detected in montmorillonites for octahedral Fe^{3+} below 0.20–0.30 per Si_8 formula unit. Our results show that: (1) this band can be observed for Fe^{3+} contents as low as 0.09 per Si_8 formula unit when continuum removal is carefully carried out; and (2) the linear relation obtained by Craciun (1984) fits our data, except for the SWa1 sample. Such deviation from linearity for Fe-rich samples was also observed by Craciun (1984).

The shift in position of the δ_{AlFeOH} band with increasing Fe content could be explained by the existence of two δ_{AlFeOH} components at ~885 and 860 cm^{-1}. As stated by Komadel *et al.* (1995), the assignment of the band located at ~850 cm^{-1} remains unclear as various propositions can be found in the literature (Table 2). Still, there is a general agreement on assigning this band to an Fe-OH or Fe-metal-OH group. We suggest the components at ~885 and 860 cm^{-1} be assigned to Fe located near *trans-* and *cis*-cavities, respectively. Based on an analogy with celadonite and glauconite (Slonimskaya *et al.*, 1986), such an assignment has already been proposed by Madejová *et al.* (1994), to explain the existence of two AlAl pairs and two FeFe pairs. In nontronites, which are *trans*-vacant (Tsipursky & Drits, 1984), the δ_{AlFeOH} can be found at positions as low as 847 cm^{-1} (e.g. Clausthal nontronite, Goodman *et al.*, 1976). On the contrary, based on the dehydroxylation temperature derived from differential thermal analysis, all

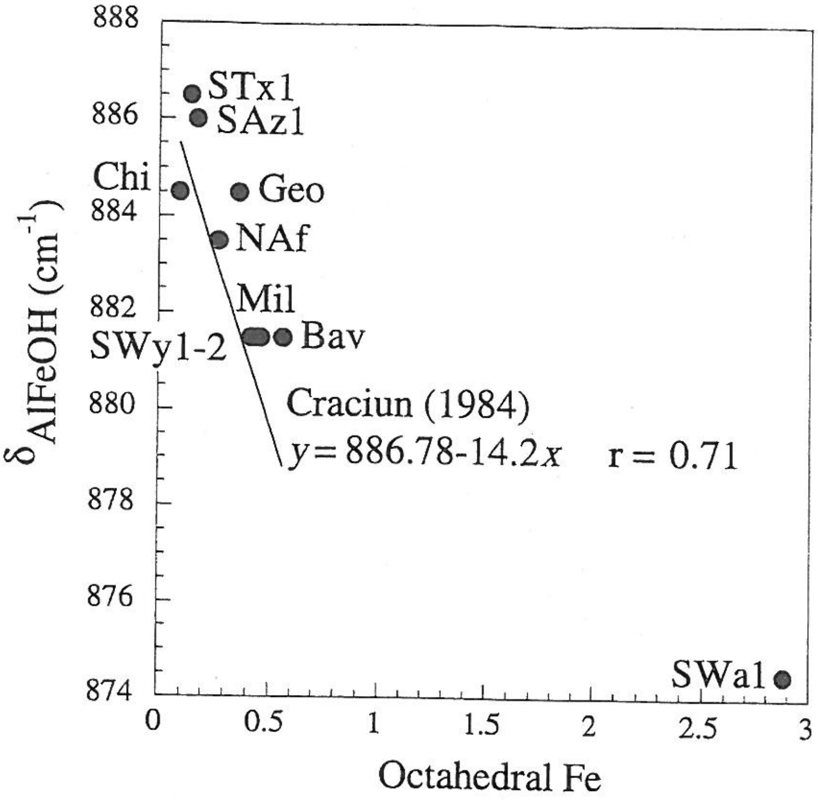

FIG. 4. Position of the δ_{AlFeOH} band as a function of octahedral Fe content for smectites. The straight line represents the equation obtained by Craciun (1984): $y = 886.78 - 14.2x$.

montmorillonite samples are preferentially *cis*-vacant (Drits *et al.*, 1995; Emmerich *et al.*, 1999). For those *cis*-vacant smectites, the δ_{AlFeOH} band is located between 886.5 and 881.5 cm^{-1} (Emmerich *et al.*, 1999). Upon heating and dehydroxylation, *cis*-cavities are increasingly occupied and concomitantly, IR bands at ~860 cm^{-1} are more marked (Emmerich *et al.*, 1999). All these experimental facts tend to confirm the proposed assignments of components at ~880 cm^{-1} to δ_{AlFeOH} in a *cis*-vacant environment and of components at ~860 cm^{-1} to δ_{AlFeOH} in a *trans*-vacant environment. According to such assignment, the shift towards lower wavenumber of the δ_{AlFeOH} band with increasing Fe content could then be due to an increased occupancy of *cis*-octahedral cavities by Fe^{3+} ions which would provoke an increase of the δ_{AlFeOH} component around 860 cm^{-1}. More detailed spectrocopic measurements are needed to confirm our interpretation.

Deconvolution results

As shown in Fig. 1b, between 950 and 750 cm^{-1} the spectra can be fitted with three main bands: δ_{AlAlOH} (917–911 cm^{-1}), δ_{AlFeOH} (878–879 cm^{-1}) and δ_{AlMgOH} (848–838 cm^{-1}). For the Washington sample, two additional bands are needed in order to obtain a good fit: δ_{FeFeOH} (815 cm^{-1}) and δ_{FeMgOH} (785 cm^{-1}). For the other samples, the components located below 800 cm^{-1} are not taken into account, as they are assigned to ν_{SiO} vibration in quartz or cristobalite (Table 2). Deconvolution results yield the area and intensity of each elementary component. As generally assumed in the literature (Slominskaya *et al.*, 1986; Besson & Drits, 1997a,b; Madejová *et al.*, 1994), the absorption coefficients of the different OH groups were considered to be invariant. Using such an assumption, the relative intensity of each band should depend directly on the chemical composition of the octahedral sheet. The relative area of each component *vs.* the amount of octahedral Al, Fe and Mg is plotted in Fig. 5 which reveals that, for each ion, the relative intensity of the various bending bands is correlated to the abundance of the cations in the octahedral sheet. A fair correlation is obtained for Al and Fe. It is even better for Mg. Such improved correlation could be due to the influence of the exchangeable Na^+ cation. Indeed, the pretreatment of the samples at 150°C for 24 h, prior to spectra acquisition, provokes a migration of dehydrated Na^+ cations towards the ditrigonal cavities, which induces some changes in the OH-bending spectra (Tettenhorst, 1962; Farmer & Russell, 1964; Calvet & Prost, 1971; Sposito *et al.*, 1983). These changes are more pronounced for the δ_{AlMgOH} band, because the exchangeable cation interacts mainly with the corresponding hydroxyl. The vicinity of the cation then creates a stable configuration for the AlMgOH hydroxyl, which yields the observed linear relation between Mg amount and IR absorbance.

For Al and Fe (Fig. 5a,b), sample SWa1 is clearly out of the correlation defined for other montmorillonites. In the case of Fe, this is logical

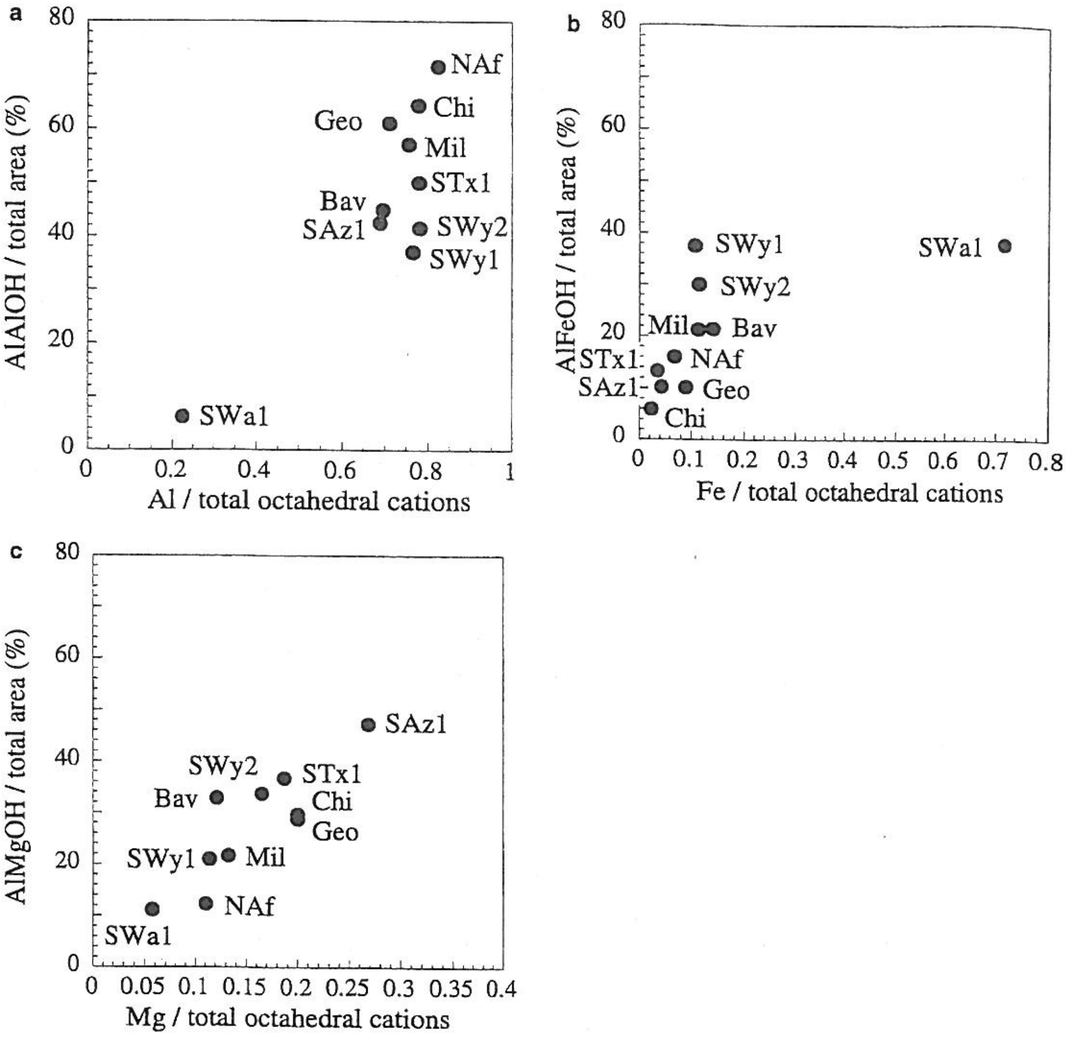

FIG. 5. Changes in the relative areas of the various OH-bending bands as a function of octahedral cation content. (*a*) δ_{AlAlOH} *vs.* Al. (*b*) δ_{AlFeOH} *vs.* Fe. (*c*) δ_{AlMgOH} *vs.* Mg.

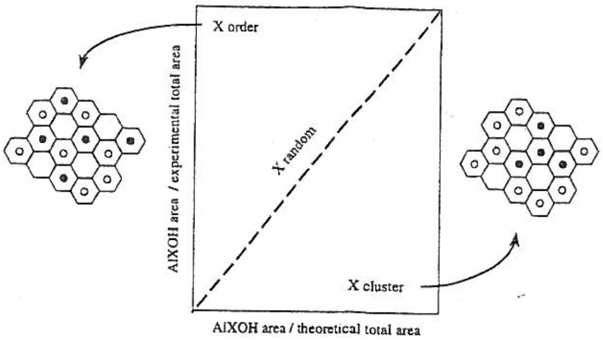

FIG. 6. Schematic representation of cation distribution in the octahedral sheet.

because AlFeOH vibrations cannot account for the total amount of Fe in this clay, as FeMgOH and FeFeOH groups were observed in the IR spectra. In the case of Al, such deviation may be tentatively explained by small changes in the absorption coefficients due to the high Fe content in Washington montmorillonite. In order to go further in our analysis of cation distribution in the octahedral sheet, we plotted the relative areas of the OH-bending bands as a function of the theoretical area that one would obtain assuming a fully random distribution of octahedral cations (Fig. 6). This random distribution was obtained simply by calculating the probabilities of the different cation pairs from chemical analysis without introducing any exclusion or clustering rules. Using such a plot, it is possible to show the tendencies for various cations to order or cluster. Indeed, if the octahedral cations are distributed according to a random pattern, the experimental points should fall along the 'random' line indicated in Fig. 6. If the points are located below this line, the probability of finding a given (different) pair of cations in neighbouring sites is less likely than in a random distribution. This reveals an indirect tendency towards clustering for two different cations (e.g. AlMg or AlFe) or towards ordering for pairs of the same cation (e.g. AlAl). On the contrary, points located above this line reveal ordering for cation pairs of two different atoms and reduced clustering for cation pairs of the same atoms.

The results of such treatment for the 10 montmorillonite samples under study are presented in Fig. 7. For δ_{AlAlOH}, the mean squared deviation, calculated taking into account all the samples, is 3.3, whereas Wyoming samples exhibit a deviation of 14.5. For δ_{AlFeOH}, similar tendencies are observed with values of 2.8 and 12.3 for all samples and Wyoming samples respectively. It is clear, therefore, that all the montmorillonites studied, except those from Wyoming, can be described using a random distribution of both the Al-Al and Al-Fe octahedral pairs (assuming a constant deviation of ±5% around the experimental results to take into account experimental errors associated with the deconvolution procedures). In the case of samples SWy1 and SWy2, the position of the points for δ_{AlAlOH} and δ_{AlFeOH} clearly reveals a strong tendency to ordering. This ordering is even more marked for sample SWy2 which exhibits the same pattern for the δ_{AlMgOH} pairs. Such ordering cannot be due only to the *cis*-vacant nature of these clays as other *cis*-vacant samples do not present the same phenomenon. Cation distribution in Wyoming montmorillonites is therefore far from being random but obeys some clear exclusion rule. A similar conclusion was reached by Madejová *et al.* (1994), for the Al-Al pairs in SWy1. It is interesting to point out that, working with synthetic dioctahedral clay samples, Decarreau *et al.* (1992) observed the tendency of Al and Fe atoms to mix rather than to segregate. In view of these results, it would certainly be fruitful to try to link this peculiar crystal chemistry of the Wyoming montmorillonites with the genetic conditions for deposit formation.

In their study, Madejová *et al.* (1994) stated that Al–Al links and Al–Mg links were favoured in the montmorillonite from Washington. In our case, this may be true for the Al–Mg links but is not observed for the Al–Al pairs. This difference in conclusion could be due to the use of the stretching region in the work by Madejová *et al.* (1994), where, as already mentioned, the presence of residual water signals can cause some inaccuracy

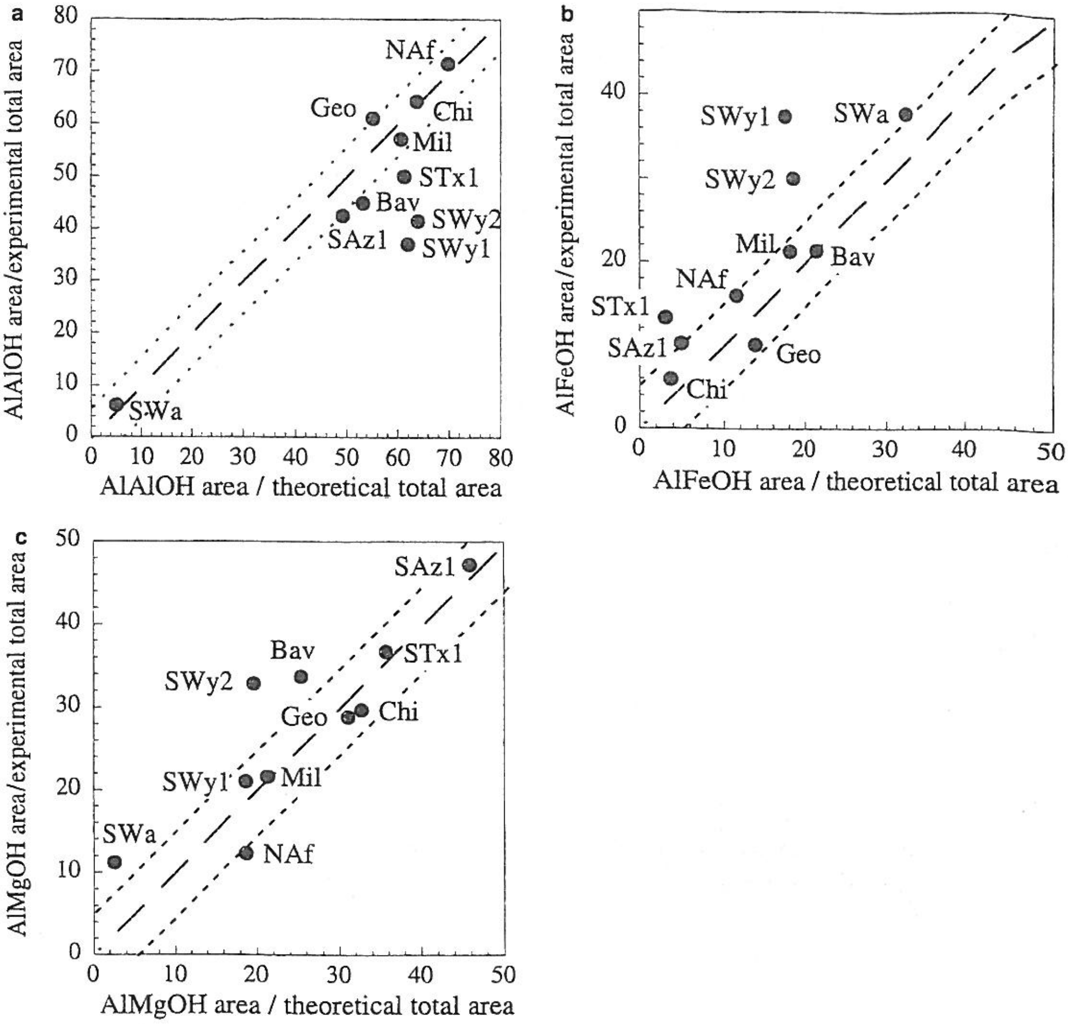

FIG. 7. Changes in the relative areas of the various OH-bending bands as a function of the theoretical areas derived from assuming a fully random distribution. (*a*) δ_{AlAlOH}. (*b*) δ_{AlFeOH}. (*c*) δ_{AlMgOH}.

in the deconvolution results. Analyses including the bending, stretching and combination bands together may bring additional insights into the cation ordering preferences for smectite clays.

CONCLUSIONS

The IR domain corresponding to OH-bending provides qualitative and quantitative information about cation distribution in the octahedral sheet even if there are obvious limitations inherent in both the baseline correction and deconvolution procedures. As already shown in other studies (Craciun, 1984), the position of the δ_{AlFeOH} IR band varies linearly with the octahedral Fe abundance. This linear relation has been extended down to very low Fe contents in this study ($\cong$ 0.09 Fe per Si_8 formula unit) and possibly is explained by an increased occupancy of *cis*-positions by Fe atoms. By comparing the specific OH populations deduced from IR experiments with a random distribution of sites, it is shown that most montmorillonite samples exhibit an approximately randomized octahedral cation distribution. One notable deviation from this rule can be found for samples from Wyoming where a strong tendency to ordering is observed. This conclusion may have important consequences for clay mineralogy, as it suggests that Wyoming montmorillonites, which are often considered as reference samples, may not be the most suitable representatives of the montmorillonite group,. at least in terms of crystal chemistry.

Such ordering may induce changes in the size and shape of clay platelets and consequently modify their macroscopic properties which could explain the remarkable rheological behaviour of samples from Wyoming compared with montmorillonites from other locations. These preliminary observations suggest that some valuable information about the physical chemistry of clay minerals may be extracted from a detailed study of their crystal chemistry. Further developments of this approach may be achieved by following two main directions. First, mapping of the octahedral sheet in montmorillonites can be greatly refined using other local spectroscopic techniques such as UV-Vis spectroscopy, Near IR, Extended X-ray Absorption Fine Structure (EXAFS), Mössbauer spectroscopy and Electronic Paramagnetic Resonance (EPR). Secondly, our understanding of the relationships between local crystal structure and macroscopic behaviour will be enhanced if the natural heterogeneity of clay minerals is taken into account. This can be achieved by local imaging and chemical analysis using microprobe techniques.

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